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# SOME GENERALIZATIONS OF THE STABILITY OF LIQUID–GAS–VAPOR SYSTEMS*

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## NOMENCLATURE

$c_p$, specific heat at constant pressure;
$G$, gas-content parameter defined in equation (5);
$g$, specific Gibbs function;
$h$, specific enthalpy;
$m$, mass;
$p$, pressure;
$p_{amb}$, ambient pressure;
$p_v$, vapor pressure evaluated at $T_0$;
$R$, equilibrium bubble radius;
$R_{in}$, stable equilibrium gas–vapor bubble radius for a given $p_{amb}$;
$R_{ms}$, maximum stable equilibrium gas–vapor bubble radius for a given $G$;
$R_0$, unstable equilibrium radius of a vapor bubble;
$R_u$, unstable equilibrium gas–vapor bubble radius for a given $P_{amb}$;
$\mathcal{R}$ gas constant on a unit mass basis;
$s$, specific entropy;
$T$, temperature ($\simeq T_{sat}$ if unspecified);
$T_{sat}$, saturation temperature at $p_{amb}$;
$V$, volume;
$\alpha$, concentration of dissolved gas in a liquid;
$\beta$, Henry's Law constant;
$\Delta a$, thermodynamic availability above a given dead state;
$\Delta G$, potential barrier to nucleation;
$\Delta\tau$, liquid superheat [$= (T_0 - T_{sat})$];
$\rho$, density;
$\sigma$, surface tension between a liquid and its vapor.

General subscripts
$a$, denoting permanent gas;
$f$, denoting saturated liquid;
$g$, denoting saturated vapor;
$l$, denoting superheated liquid;
$o$, denoting the locally superheated condition.

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## INTRODUCTION

THE literatures of cavitation and of boiling have produced many worthwhile analyses [e.g. 1–6] on aspects of the stability of superheated and supersaturated liquid–gas–vapor systems. This note extends certain of this material to provide general equations and curves describing the limits of stability of such systems.

Bubbles grow spontaneously in supersaturated liquids because of mass diffusion into the liquid–gas interface, and in superheated liquids because of heat diffusion into the liquid–vapor interface with evaporation at the interface. In either case, a knowledge of the conditions on bubble stability with respect to growth or collapse aids in predicting growth inception and fixing initial conditions on dynamical equations.

## THE PHYSICAL CONDITIONS ON STABILITY

A superheated or supersaturated liquid is in a condition of metastable equilibrium and can be perturbed into a state of unstable equilibrium by adding an appropriate spherical gas–vapor bubble. A static balance on such a perturbation bubble requires that:

$$p_a - p_{amb} + p_v = (2\sigma/R) \tag{1}$$

When there is a constant mass of permanent ideal gas, $m_a$, in the bubble:

$$p_a = \frac{3m_a \mathcal{R} T}{4\pi R^3} \tag{2}$$

but when mass diffusion is important:

$$p_a = \alpha\,\beta \tag{3}$$

In the former case:

$$\frac{(p_{amb} - p_v)}{2\sigma} = \frac{G}{R^3} - \frac{1}{R} \tag{4}$$

where: The *gas-content parameter*, $G \equiv \dfrac{3m_a \mathcal{R} T}{8\pi\,\sigma}$ (5)

Figure 1 displays equation (4) for 21 values of $G$, in completely general form. Figure 1 is similar to a curve

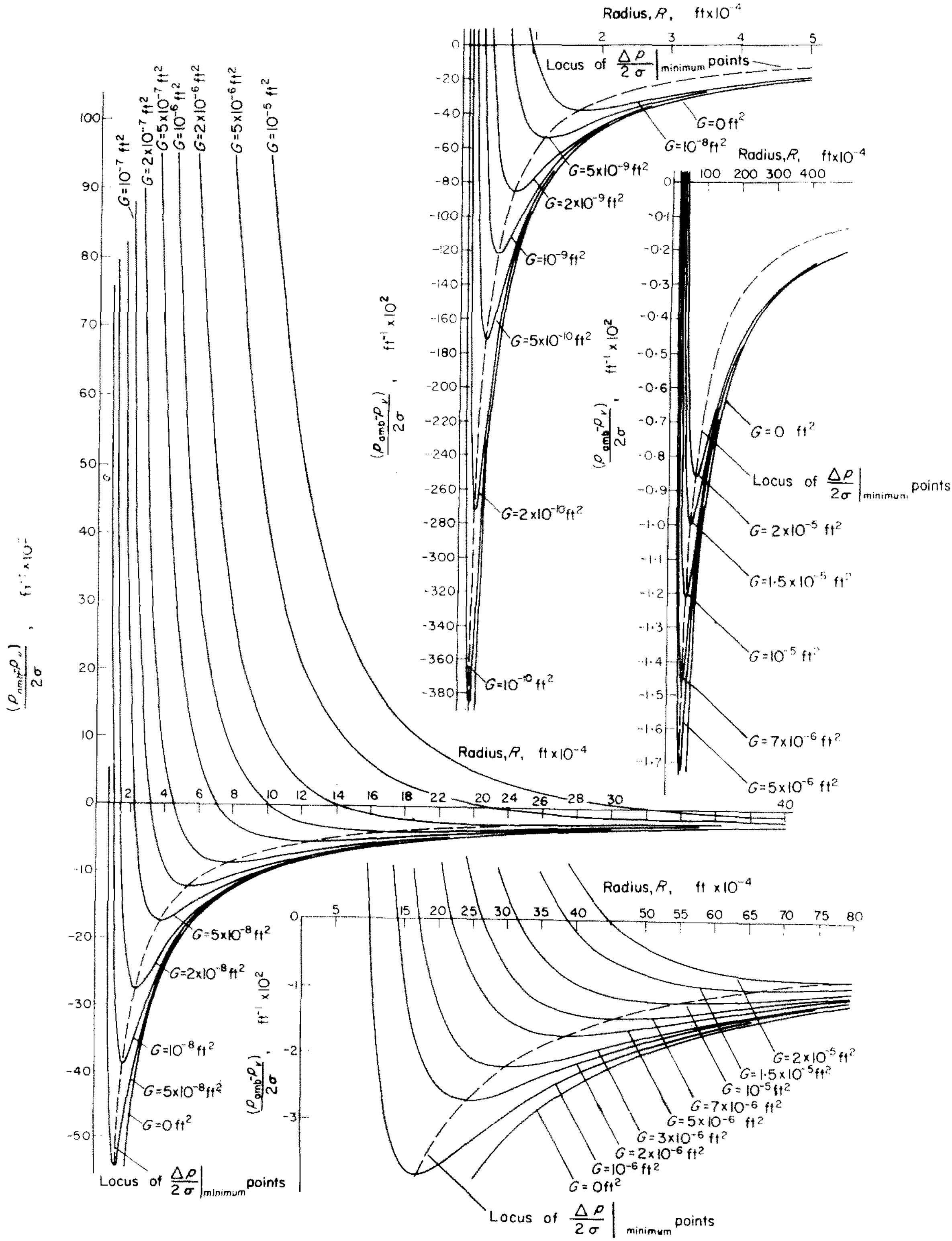

FIG. 1. Generalized dependence of $(p_{amb} - p_v)/2\sigma$ on equilibrium gas–vapor bubble radius, for values of gas content parameter, $G$.

given by Daily and Johnson [3], for the particular case of water at 68°F.

The thermodynamic criterion for mechanical stability specifies that a system is stable if for all possible variations of its state:

$$\left.\frac{\partial p}{\partial v}\right|_T < 0 \tag{6}$$

thus the descending lines of constant $G$ in Fig. 1 represent stable states and the ascending lines represent unstable conditions. The maximum stable radius, $R_{ms}$, for a given $G$ is obtained by maximizing $R$ in equation (4) (see, e.g. [6]):

$$R_{ms} = \frac{4\sigma}{3(p_v - p_{amb})} \tag{7}$$

The radius, $R_0$, of a pure vapor bubble at the same pressure is obtained by setting $G = 0$ in equation (4):

$$R_0 = \frac{2\sigma}{(p_v - p_{amb})} \tag{8}$$

All possible unstable equilibrium radii, as $G$ is diminished at constant $p_v$, fall between $R_{ms}$ and $R_0$ (see Fig. 2).

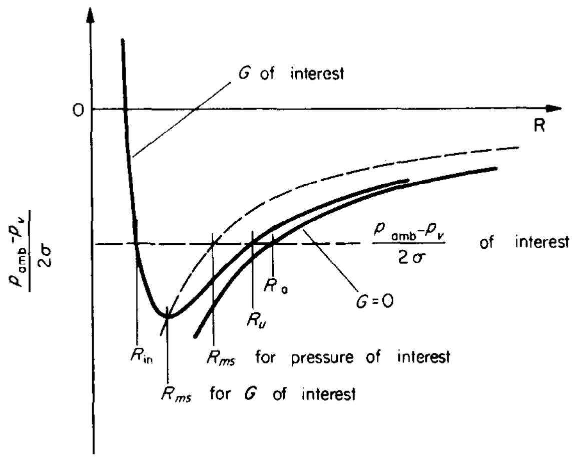


FIG. 2. Detail of effect of gas content upon bubble equilibrium.

When equilibrium is determined by mass diffusion, equation (1) becomes:

$$\frac{p_{amb} - p_v}{p_{amb}} = \frac{\alpha\,\beta}{p_{amb}} - \frac{2\sigma}{p_{amb}\,R} \tag{9}$$

Equations (9) and (7) are both plotted in general co-ordinates in Fig. 3.*

* Strasberg [2] gave similar curves for an (unspecified) particular situation, but he did not show how equation (9) behaved in the neighborhood of equation (7) in his plot.

Spontaneous growth by mass diffusion will proceed along a horizontal path to the right, from any initial point above the plot of equation (7), in Fig. 3. If $(p_{amb} - p_v)$ is negative such a bubble will become unstable with respect to growth by heat diffusion when its radius attains the value specified by equation (7). Since predictions of rates of bubble growth by mass diffusion [7] and by heat diffusion [8, 9] reveal the latter to be far more rapid, mass diffusion must usually be ignored when $R \geqslant R_{ms}$. All growth to the right of equation (7) will accordingly be vaporous.

## THERMODYNAMIC MEASURES OF STABILITY

Frenkel [10] gives the "potential barrier" to nucleation of pure vapor bubbles, $\Delta G$†, as:

$$\Delta G = (4\pi/3)\,\sigma\,R_0^2 \tag{10}$$

this is a measure of the "free" mechanical energy needed to perturb a metastable liquid into instability.

When undissolved permanent gas is present in the liquid it should diminish $\Delta G$. In this case, $\Delta G$ can be computed as the change in the Gibbs function between the stable gas–vapor bubble of initial radius, $R_{in}$, and the unstable gas–vapor bubble of radius, $R_u$, at the same $p_{amb}$ (see Fig. 2).

$$\Delta G = \Big[m_g g_g + m_l g_l + m_a g_a + 4\pi\sigma R^2\Big]_{R_{in}}^{R_u} \tag{11}$$

The system considered includes the bubble and an amount of liquid surrounding it initially. The term $4\pi\sigma R^2$ is the surface energy of the interface. Equation (11) simplifies to:

$$\Delta G = (g_g - g_l)\Big[m_g\Big]_{R_{in}}^{R_u} + 4\pi\,\sigma\,(R_u^2 - R_{in}^2) + m_a \int_{R_{in}}^{R_u} \frac{\mathrm{d}p_a}{\rho_a} \tag{12}$$

Use of the ideal gas law ($\rho_a = p_a/\mathscr{R}T$) and equation (2) lead to:

$$m_a \int_{R_u}^{R_{in}} \frac{\mathrm{d}p_a}{\rho_a} = -\,3m_a\,\mathscr{R}T \ln\frac{R_u}{R_{in}} \tag{13}$$

furthermore:

$$\Big[m_g\Big]_{R_u}^{R_{in}} = \frac{4\pi}{3}\,\rho_g\,(R_u^3 - R_{in}^3) \tag{14}$$

The evaluation of $(g_g - g_l)$ requires the use of the condition for thermal equilibrium:

$$[\mathrm{d}\ (\text{Gibbs function})_{T,\,p}] = 0 \tag{15}$$

which, applied to equation (11) with the understanding that $g_g$, $g_l$, and $m_a$ are constants, and $\mathrm{d}m_g = 4\,\pi\rho_g\,R^2\,\mathrm{d}R$, gives:

$$(g_g - g_l)4\pi\rho_g R^2\,\mathrm{d}R + (m_a/\rho_a)\,\mathrm{d}p_a + 8\,\pi\,\sigma\,R\,\mathrm{d}R = 0 \tag{16}$$

† $\Delta G$ is not to be confused with $G$, nor to be interpreted as a change in the gas-content parameter.

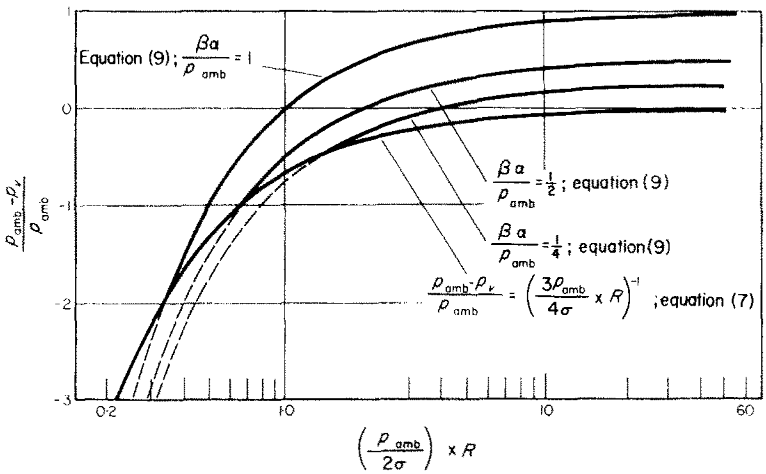


FIG. 3. The region of mass diffusion controlled gas-vapor bubble instability.

Equation (2) and the ideal gas law eliminate $p_a$ and $\rho_a$ from equation (16), whence:

$$(g_g - g_l) = \frac{(3m_a \mathscr{R}T/R^2) - 8\pi\sigma}{4\pi R \rho_g} \tag{17}$$

Substitution of equations (17), (14), (13), and (5) into equation (12) gives the dimensionless form of $\Delta G$ for a gas-vapor bubble:*

$$\frac{3\Delta G}{8\pi\sigma} = (G - R_u^2)\left[1 - \left(\frac{R_{\text{in}}}{R_u}\right)^3\right] + \frac{3}{2}(R_u^2 - R_{\text{in}}^2) - 3G\ln\frac{R_u}{R_{\text{in}}} \tag{18}$$

which reduces to equation (10) when $G = 0$.

Figure 4 displays equation (18) in general co-ordinates and shows quantitatively how gas bubbles provide part or all of the "triggering" perturbation needed to produce bubble growth.

A measure of the extent to which a superheated liquid has departed from a stable equilibrium, is given by the work that the system could do upon its surroundings in returning to equilibrium. This is equal to the availability

* Nesis and Frenkel [11] expressed the potential barrier to the formation of a bubble in a homogeneous gas–liquid solution in terms of the mole fractions of gas and vapor in the bubble. They used this expression to identify the unstable equilibrium radius.

The present study, on the other hand, has assumed that both the stable and unstable equilibrium radii are known from a macroscopic analysis, and has computed the $\Delta G$ required to perturb the stable radius into an unstable condition. This $\Delta G$ is accordingly smaller than Nesis and Frenkel's value.

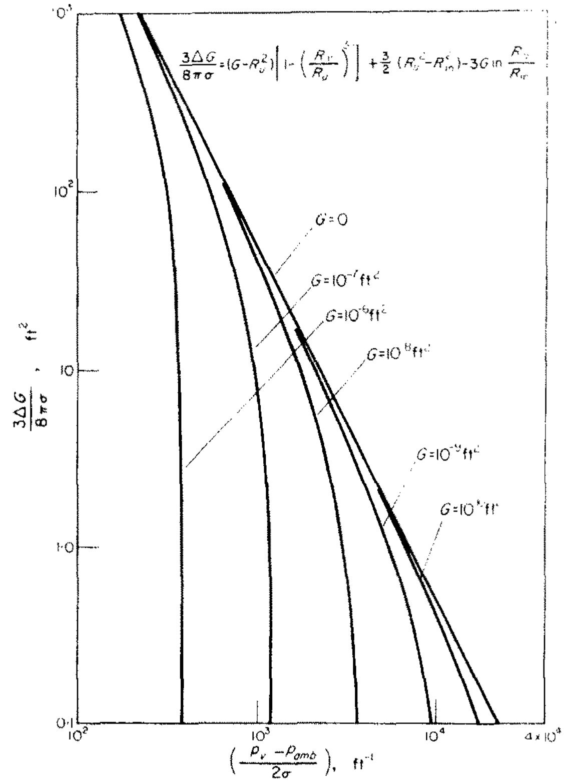


FIG. 4. The effect of liquid superheat (as characterized by $(p_v - p_{amb})/2\sigma$) and gas content upon the potential barrier to nucleation.

of the system, $\Delta a$, above $p_{amb}$ and $T_{sat}$. In this isobaric case:

$$\Delta a = (h_0 - h_f) - T_{sat}(s_0 - s_f) \tag{19}$$

but $c_p$ should be nearly constant in the temperature range of interest, so:

$$\Delta a = c_p\left(\Delta\tau - T_{sat}\ln\frac{T_0}{T_{sat}}\right) \tag{20}$$

Since $T_0/T_{sat}$ is slightly greater than unity,

$$\ln(T_0/T_{sat}) \simeq \left(\frac{T_0}{T_{sat}} - 1\right) - \frac{1}{2}\left(\frac{T_0}{T_{sat}} - 1\right)^2 \tag{21}$$

whence:

$$\Delta a = \frac{c_p}{2\,T_{sat}}\,\Delta\tau^2 \tag{22}$$

The quantity $\Delta a$ specifies the capacity of a unit mass of superheated liquid for disrupting the system when nucleation is triggered. That $\Delta a$ increases with the square of the superheat, shows for example why bumping in a smooth test tube is far more violent than boiling in a rough tea-kettle even though it occurs at only slightly higher superheats.

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# FURTHER CALCULATIONS ON THE HEAT TRANSFER WITH TURBULENT FLOW BETWEEN PARALLEL PLATES

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## NOMENCLATURE

$y_0$, half parallel plate gap;
$y^+$, dimensionless $y$ co-ordinate;
$\epsilon_H$, eddy diffusivity for heat;
$\epsilon_m$, eddy diffusivity for momentum;
$\beta$, ratio of heat inputs at walls.

## INTRODUCTION

The calculations described in [1] have been repeated with the object of determining the order of change in the heat-transfer results caused by different choices of certain basic assumptions in the analysis. In addition the calculations have been extended to a wider range of Prandtl numbers.

In the previous work [1] it was assumed that the eddy diffusivity of momentum was constant over the middle half of the passage (i.e. between $y_0^+/2$ and $3y_0^+/2$). That is, constant at the maximum value as given by Deissler's form of the eddy diffusivity variation. A reconsideration of the available experimental work, particularly that of Corcoran *et al.*, referred to in [1], showed that a more realistic assumption is to take the eddy diffusivity constant over the middle third of the passage (i.e. between $2y_0^+/3$ and $4y_0^+/3$). This modification was made but, in fact, has a negligible effect on any of the heat-transfer results.

It was also assumed in [1] that the ratio of the eddy diffusivities for momentum and heat was unity. In this extension the ratio has been calculated from the expressions proposed by Azer and Chao [2].

Results were given in the previous article for Prandtl numbers of 0·1, 1·0 and 10. This work includes the further eigenvalues for Prandtl numbers 0·01 and 0·7 and some